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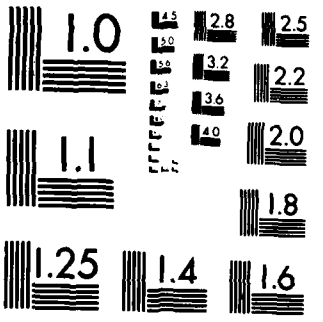

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Reply to the Comments of G. W. Bryant on "Laser Excitation of Surface Electronic States for a One-Dimensional Semiconductor"

by

William C. Murphy, Ki-Tung Lee
and Thomas F. George

Prepared for Publication

in

Surface Science

Department of Chemistry
University of Rochester
Rochester, New York 14627

February 1982

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A semiconductor modeled by a finite one-dimensional chain is shown to have either a continuous or discrete number of surface states The exact number is determined by the choice of phase factors. Laser-induced charge transfer of electrons from the bulk to these surface states is also shown to be a maximum at the band edge.

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Abstract

A semiconductor modeled by a finite one-dimensional chain is shown to have either a continuous or discrete number of surface states. The exact number is determined by the choice of phase factors. Laser-induced charge transfer of electrons from the bulk to these surface states is also shown to be a maximum at the band edge.

Recently, we presented a paper[1] on the laser excitation of electrons into the surface states of a one-dimensional semiconductor. Bryant[2] has questioned some of our conclusions because he claims a one-dimensional chain can only have a discrete surface state, whereas we had a *continuum* of surface states. This difference can be reconciled by a careful determination of the surface states.

For simplicity, we employed plane waves in the basis set for the internal wavefunction of our chain. Since the existence of a surface will lead to reflected waves, a more exact basis should include a contribution from the complex conjugate. Therefore, in trigonometric representation, the basis state will be[3]

$$\phi(z) = C \sin(kz + \theta_k), \tag{1}$$

where C is a normalization constant, k is the wavevector of the electron, and θ_k is the phase factor. Bryant has assumed that both the square well and lattice potential are symmetric about zero. Under these conditions the phase will be either zero or $\pi/2$. However, we initially made no such assumptions and proceeded from the general solution, eq.(1), to obtain the wavefunction for the surface states.

To determine the basis for these surface states, we now replace the wavevector k with $k + i\kappa$. However, since θ_k is dependent on k, we must in general assume that it is also complex; therefore, we replace θ_k by $\alpha + i\beta$. Using this expression, some algebra[3] yields the surface state

$$\psi(z) = C_s\, e^{-\kappa z} \sin(\tfrac{q}{2}z + \theta_\kappa), \tag{2}$$

$$\theta_\kappa = \alpha + \delta, \tag{3}$$

where C_s is the surface state normalization constant and θ_κ is the phase factor. The constant δ is obtained from the secular equations:[4]

$$\sin 2\delta = \frac{g\kappa}{V}, \tag{4}$$

where g is the reciprocal lattice vector and V is the Fourier component of the lattice potential. Because of the boundary conditions, the value of θ_κ is also determined:[3]

$$\tan \theta_\kappa = \frac{g/2}{\kappa - q}, \tag{5}$$

where q is the exponential damping in the external wavefunction. In Bryant's analysis α was assumed to be zero. The discreteness of the surface state state would arise by requiring eqs.(3), (4) and (5) to hold simultaneously. In our work, however, we made no assumptions about α; the value of α was completely determined by eq.(3). Consequently, our surface states formed a continuum. So the question about discrete or continuous surface states must be resolved around the physical nature of surface states. Since these states are discrete for any given value of the parallel wavevector, a discrete view would seem to be applicable. However, the surface states can fall at any energy in the gap when all values of the parallel wavevector are considered, so a continuum model could also be applied.[5] The failure of the one-dimensional model to predict both aspects of the three-dimensional surface states is at the heart of the problem. The decision between continuous and discrete surface states within a one-dimensional framework is thus arbitrary.

Bryant further claimed that the selection rule requiring conservation of the real part of the wavevector in surface transitions is invalid. It is true that the rule is only exactly correct when the imaginary part of the wavevector is zero. However, the maximum value of κ is $|2V|/g$, and thus the

largest imaginary-to-real ratio for the wavevector would be $|2V|/0.5g^2$. This is essentially the ratio of the energy gap to the width of the valence band, and, for wide-band semiconductors such as silicon, the maximum value of the imaginary-to-real component of the wavevector would be about 0.05. Consequently, since the imaginary component is never very large, the selection rule should approximately hold.

If we examine the basis set, eq.(1), we see that the states can either be odd or even in terms of the wavevector k. The bulk wave function can therefore be written in odd,

$$\psi(z) \sim \sin(kz + \theta_k) + C_{k-g} \sin[(k-g) + \theta_{k-g}] \ , \tag{6}$$

or even form,

$$\psi(z) \sim \cos(kz + \theta_k) + C_{k-g} \cos[(k-g) + \theta_{k-g}] \ . \tag{7}$$

In both of these expressions the phase factor is even in k. At $k = g/2$ the constant becomes

$$C_{-g/2} = -\frac{V}{|V|} \ . \tag{8}$$

Thus the bulk wave function composed of an even-k basis set will have a maximum amplitude and produce a maximum transition rate at the band edge for $V < 0$. For $V > 0$, the odd-k basis will produce the maximum transition rate. In both of these cases, the transition rate does not vanish at $k = g/2$ as Bryant claims, and thus the selection rule would approximately hold. For $V > 0$ with even-k basis and $V < 0$ with odd-k basis, there is no wavefunction at the band edge, and subsequently it is not considered.

In conclusion, we see that there can indeed be a one-dimensional chain with a continuum of surface states. Furthermore, laser-induced transitions

to these states will reach a maximum from the bulk states at $k = g/2$. The discrete surface state approach to this problem, however, can be useful. Nonetheless, with either discrete or continuous surface states, our contention that laser-induced surface charge can alter surface processes stands![1,3] A more complete analysis which will resolve the ambiguities of the one-dimensional model would involve higher dimensions and has been in progress within our research group since the past summer.

Acknowledgments

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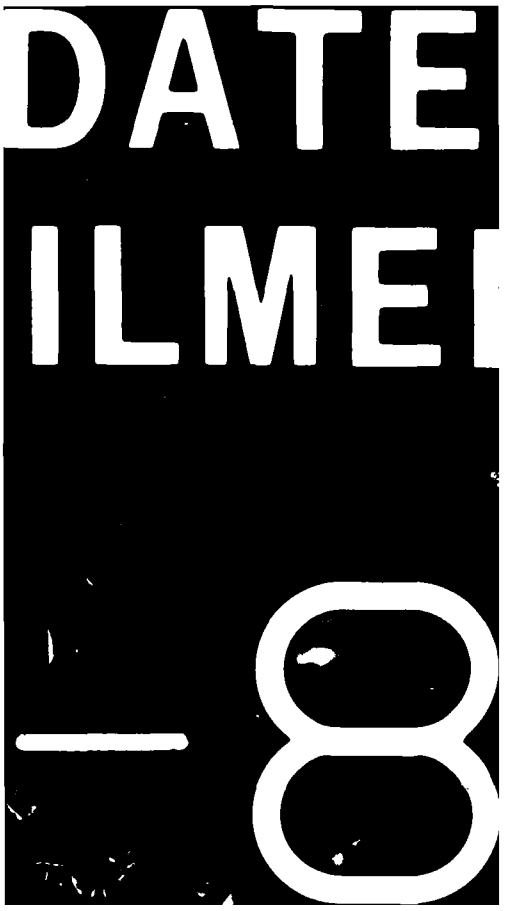
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